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Structure and tribological properties of carbon based nanocomposites grown by TVA method

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The aim of this paper is to report on the synthesis and the characterization of nanocomposite carbon-metal films obtained by the Thermionic Vacuum Arc (TVA) method. Surface morphologies and microstructure of C-Me thin films were examined using TEM and SEM provided by Philips ESEM 120 device equipped with EDS spectrometer. The tribological behavior was analyzed by a CSM-Switzerland, ball-on-disc tribometer. The coefficients of friction were found to be influenced by the percent of carbon atoms in the nanocomposite, depending on the experimental conditions.

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1. Introduction

Deposition processes of multilayer or multi-element nanocomposite coating must have several different metal vapor or sputtering sources providing highly ionized and activated metal vapor plasma. Free coating droplets and growth without defects is critically important to achieve high performance of tribological characteristics and wear resistive coatings [1] - [4]. Carbon-metal (C-Me) deposition is interesting for the following reasons: the ability of manipulating the tribological properties by infiltrating metal inclusions inside the films of amorphous carbon as well as the ability of lowering the stress and improving the adhesion of the prepared films.

Thermionic Vacuum Arc (TVA) is an original type of discharge first reported in 1984, which ignites in the vapors of the anode material, continuously generated by the electron bombardment of the anode in high vacuum conditions [5]. The electrons, emitted from a heated tungsten cathode, are accelerated towards the anode, by a d.c. high voltage applied across the electrodes. At switch on, the anode material first melts and afterwards starts to boil, a steady state metal vapor atoms density being established in the interelectrodic space. At further increase of the applied high voltage, a bright and stable metal vapor discharge is established.

TVA can be used to deposit thin films of various materials like alloys, ceramics, DLC (Diamond Like Carbon) *or* refractory metals such as W, Mo, Ta, Nb, Re and B, due to the high density of the power on the unit surface of the evaporating material [6] - [9].

The aim of this paper is to characterize the nanostructured carbon-metal bilayers deposited by Thermionic Vacuum Arc (TVA) technology in a special two electron guns configuration.

2. Experimental

TVA method of deposition the carbon-metal films is a genuine technology of coating varied components. In this method, the deposition takes place in high vacuum conditions, without the presence of any gas as in the case of other deposition methods (Ar for magnetron sputtering), excepting the vapors of the material from the anode.

TVA method allows the simultaneous deposition of different materials, providing the possibility of obtaining multi-component thin films in a special two electron guns configuration (Fig. 1). The electron guns are symmetrically arranged with respect to the substrate – glass and stainless steel –between the two anodes. The electric arc ignites between the cathode - a heated filament inside of a Wehnelt cylinder - and the anode material carbon or metal (Ag, Al) continuously evaporated by the electrons accelerated at high voltage and incident of the anode. The anode temperature of the each element was adjusted in order to have comparable evaporation rates.

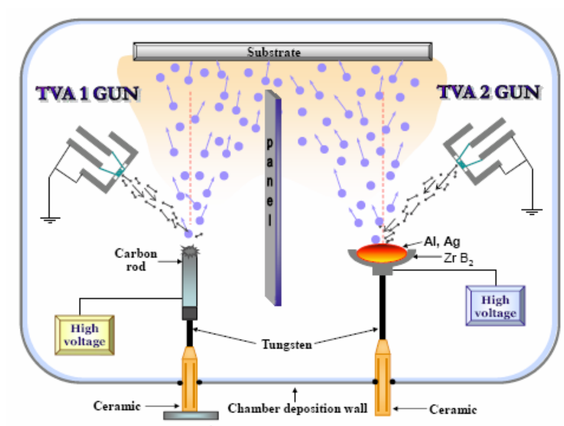


Fig. 1. Electrodes set-up for simultaneous deposition of two materials on the same sample.

Since the deposition rate decreases with the square of the anode-substrate distance, we can expect that the samples situated close to the C anode to contain higher C concentration relative to the metals (Ag and Al).

The filament heating current is I_f = 48 A, at a deposition rate of 3Å/s. The pressure during the discharge process is about $2x10^{-4}$ – $1x10^{-3}$ Pa. The applied high voltage ranges between 1.5 kV to 2.5 kV for each system anode – cathode. The panel from the middle of this arrangement plays the role to avoid the interactions between the two plasmas.

The substrates are fixed on a stainless steel planar holder above the evaporation sources. The distribution of samples on the holder is indicated in Fig. 2 as follows: there are 5 pieces of stainless steel discs, 5 pieces of optical glass and 8 pieces of glass in the middle of the holder. The thickness monitor was used to control the layer thickness from different evaporation sources. Other distances maintained in this experimental configuration are illustrated as well in the same figure.

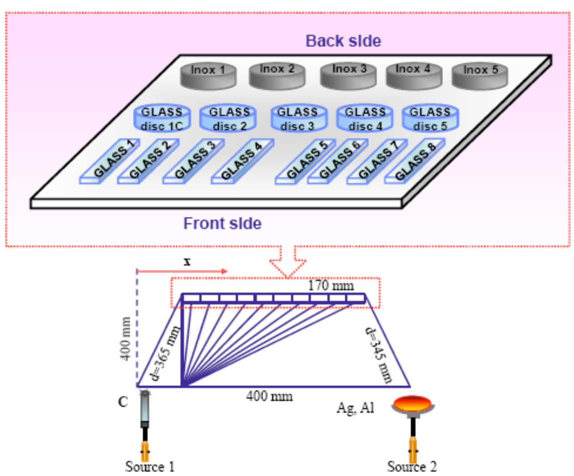


Fig. 2. Sample position on holder for C-Ag discharge.

The nanocomposites were investigated using Transmission Electron Microscopy (TEM). Analyses were performed on a Philips CM 120 ST (120 kV) TEM provided with HR-TEM facility capable of obtaining a resolution of 1.4 Å and a magnification of 1.2 M. The tribological behavior was analyzed by a CSM-Switzerland, ball-on-disc tribometer with sapphire ball.

3. Results and discussion

A ball-on-disc friction tester was used for the friction tests. A 1N normal load was loaded on the ball (diameter 6 mm; ball made of AISI 52100 hardened bearing steel) in contact with the rotating disc (sample) at a sliding speed in dry conditions of 0.1 meter per second.

Fig. 3 shows the frictional behavior of the C-Ag and C-Al films prepared by TVA method. One can observe a maximum coefficient of friction for the C-Ag 3 sample (μ=0.40). Lower content of Ag leads to a decreasing of the coefficient of friction, but the adherence of the film was low.

Higher adherence of the C-Ag films was obtained at higher concentration of the Ag, a minimum coefficient of friction being achieved at lower atomic percent concentration of Ag in C matrix.

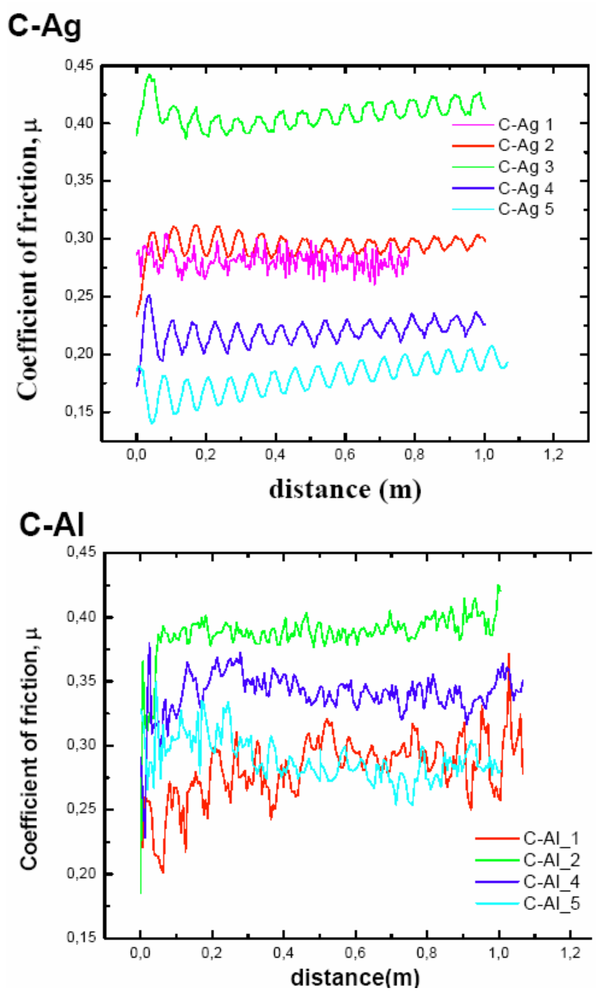
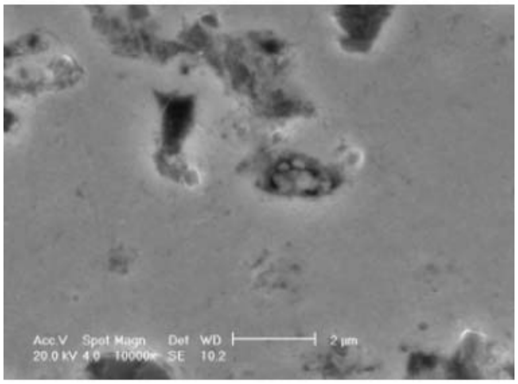


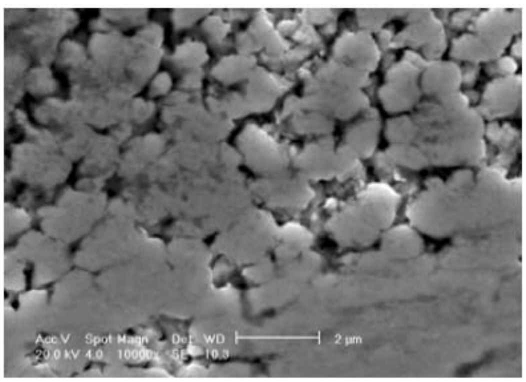
Fig. 3. Tribological characterization of C-Ag and C-Al thin films.

The addition of metal atoms in the carbon network could be another way to reduce the carbon film stress. The relaxation of stress appears associated to other effects owing to formation of metallic crystalline domains, partial graphitization and separation of phases during growth and to the formation of metal – carbon nanocomposites [10].



C-Ag 1

Element	Wt %	At %
C	3.46	23.62
Mg	1.16	3.91
Ag	95.38	72.47
Total	100	100



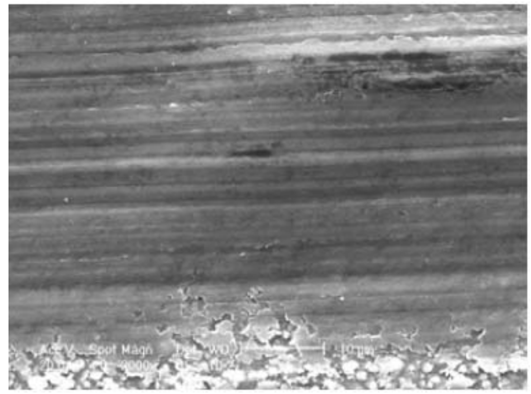
C-Ag 3

Element	Wt %	At %
C	3.27	22.68
Mg	1.02	3.49
Ag	95.71	73.83
Total	100	100

Fig. 4. SEM image of the Ag-1 and Ag -3 samples after the friction test (image up) and the relative elemental composition of the coating (tables down).

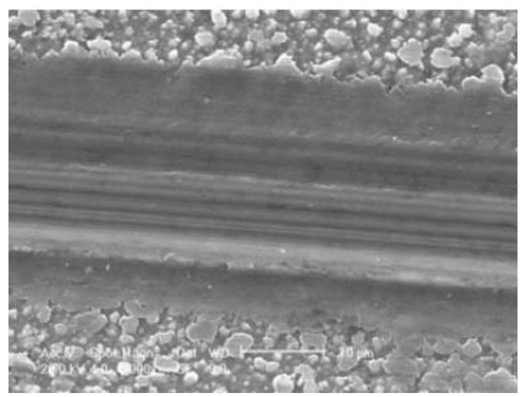
SEM images of the C-Ag films provided in Fig. 4 after the friction test revealed a very good smoothness as well as compactness. The tables under the figures illustrate the relative elemental compositions of the deposited coatings as determined by EDS analysis, in weight and atomic percentages. A slightly less content of Ag in the C matrix decreases the value of the friction coefficient (μ = 0.29).

Similar tribological behavior is noticed for C-Al also, the coefficient of friction first increase for higher percentage of Al on amorphous carbon. The maximum coefficient of friction was obtained at 25% of Al in C matrix, carbon film suffers a stress reduction when aluminum was added, inducing thus a significant improvement in film adhesion. This feature was confirmed by SEM (Fig 5) even if the scales in SEM images in figures 4 and 5 differ by a factor 5.



C-Al 1

Element	Wt %	At %
C K	13.76	26.72
O K	1.07	1.56
AlK	80.77	69.83
CrK	1.45	0.65
FeK	2.95	1.23
Total	100	100

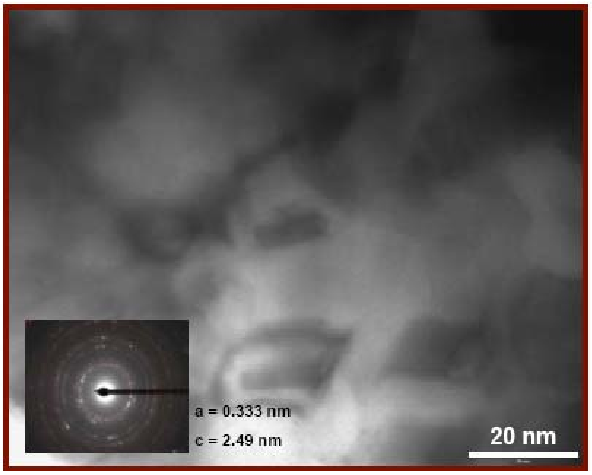


C-Al 2

Element	Wt %	At %
C K	17.86	33.17
O K	2.84	3.96
AlK	72.85	60.24
CrK	1.73	0.74
FeK	4.73	1.89
Total	100	100

Fig. 5. SEM image of the C-Al 1 and C-Al 2 samples after the friction test (image up) and the relative elemental composition of the coating (tables down).

HRTEM images (Fig. 6) reveal that C-Me structures consist of a distribution of nanocrystallites embedded within an amorphous matrix [11]. SAED performed on the silver containing nanostructures have indicated the presence of the well-defined rings, with 10 nm diameters (inset of the fig. 6 – right).



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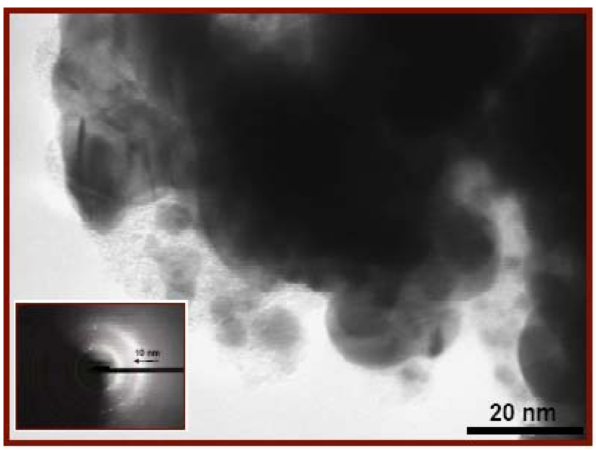

b

Fig. 6. HRTEM images of the C-Al film (a) and C-Ag (b) SAED in insets.

Electron diffraction performed on the C-Al nanostructures provided also very well-defined rings C-Al film (inset of the fig. 6 – left) with a d-spacing corresponding to a rhomboedral structure space group R-3m with a = 0.333 nm and c = 2.49 nm.

4. Conclusions

The combined deposition of carbon and metal improves basically the film adhesion and the friction coefficient. The structure of C-Me films changes with metal and its content, as verified by TEM and EDS analysis. HRTEM images and SAED reveal that C-Me structures consist on a distribution of nanocrystallites embedded within an amorphous matrix. C-Me films are suitable for surface coatings applications requiring low roughness, good smoothness and low friction coefficient.

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